



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Removal of Nickel and Vanadium From Heavy Crude Oils by Exchange Reactions

J. G. Reynolds

January 21, 2004

ACS National Meeting
Anaheim, CA, United States
February 9, 2004 through February 13, 2004

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

REMOVAL OF NICKEL AND VANADIUM FROM HEAVY CRUDE OILS BY EXCHANGE REACTIONS

John G. Reynolds

Forensic Science Center
University of California
Lawrence Livermore National Laboratory
P. O. Box 808, L-178
Livermore, CA 94551

Introduction

Current Methods of Heavy Crude Oil Processing. The upgrading of heavy crude oil occurs generally by either hydrogen addition- or carbon rejection-type processes¹. Hydrotreating is attractive because US refineries have moderately high capacity, but it is costly because it requires added hydrogen, requires appropriate metallurgy to handle the severity of conditions (high temperature and pressure), and, because of poor catalyst lifetimes (because of high metals in heavy crude oils), has high catalyst costs and non-productive downtime. In addition, with heavy crude oils, boiling point reduction is necessary for conversion to transportation fuels, so an additional cracking step is required.

Hydroconversion circumvents this cracking problem. However, similar problems to hydrotreating are encountered, such as hydrogen and metallurgy costs, with the additional problems of technology development (just beginning to become commercially available), and capital equipment investment.

Fluidized cat cracking (FCC) is also attractive because US refineries have very high capacity. Process wise, it is ideal because of the cracking step necessary to produce light components. However, FCC catalysts are notoriously metals intolerant (although new generations of RFCC catalysts show some promise), and with high S and N contents of heavy feeds, high SO_x and NO_x emissions during catalyst regeneration can be costly to abate.

Coking is also an attractive upgrading method for heavy crude oils. The US has very high capacity and more units are relatively cheap to build because severe-service metallurgy is not required. The drawbacks include poor quality products such as coke and coker gas oils, and fairly large yield losses due to the carbon rejection through coke.

Pretreatment of Heavy Crude Oils to Remove Metals.

The high metals levels of heavy crude oils currently necessitate the processing to be costly, either through the high costs of hydrogen addition or high yield loss due to carbon rejection. If metals could be removed in a pretreatment step before the heavy crude oil enters processing streams, then heavy crude oils could be more cost effectively processed by traditional methods. Hydrotreating could be utilized to a greater extent to remove the high S and N levels (for which the catalysts are specifically designed) without the quick deactivation by metals poisoning. Very-active zeolites could be used in FCC for the extensive cracking needed for boiling point reduction, and coking could be used less because the other processes could be used more, therefore avoiding such high carbon yield losses to coking. Hydroconversion units may not have to be built avoiding high capital expenditure.

The approach to the pretreatment step for metals removal can be by various methods. In this report, surrogate metal solutions containing the metal bound as petroporphyrin, or petroporphyrin fractions isolated from heavy crude oils are treated with a variety of chemical agents, and then washed with aqueous solutions to remove the metals.

Experimental

Reagents. Ethylenediamine tetraacetic acid (EDTA) •2H₂O was purchased from Sigma; disodium salt of EDTA (Na₂EDTA), nitrilotriacetic acid (NTA), disodium NTA (Na₂NTA), diethylenetriamine pentaacetic acid (DEPTA), N-(2-hydroxyethyl)ethylene diamine triacetic acid (N-HEEDTA), trisodium N-HEEDTA (Na₃N-HEEDTA), benzoic acid, malic acid, malonic acid, maleic acid, maleic anhydride, fumaric acid, oxalic acid, triethylcitrate, hexamethylenetetraamine (HMTA), phthalocyanine, tetraphenyl porphyrin, catechol, di-*t*-butyl catechol, coumarin, formic acid, diethyldithiocarbamate sodium salt (Et₂dtcNa)(H₂O)₃, Et₂dtc diethylammonium salt (Et₂dtcEt₂NH₂), *t*-butyl hydroperoxide, cumene hydroperoxide, peroxyacetic acid, sodium sulfide nonahydrate (Na₂S•9H₂O), Fuller's Earth, bentonite, montmorillonite, pyridine-N-oxide, 3-pyridylcarbinol-N-oxide, acetone oxime, titanium tetrakis-*i*-propoxide (Ti(OCH(CH₃)₂)₄), titanium oxide acetyl acetonate (TiO(acac)₂), fluorosulfonic acid (FSO₃H), trifluoro sulfonic acid (CF₃SO₃H), DMF, and 1-MN were purchased from Aldrich Chemical Co; tartaric acid was purchased from Baker Chemical Co.; CH₂Cl₂, toluene, and methanol were purchased from Baxter Scientific; DMF was purchased from EM Scientific; carbon dioxide, carbon monoxide, oxygen were purchased from Matheson; titanium dioxide (TiO₂), was purchased from Allied Chemical Co; VO(etio) and Ni(etio), were purchased from Midcentury Chemical Co., Posen, IL. 1,4,8,11-tetraazacyclotetradecane (Cyclam) was prepared by the method of Richman and Atkins².

Reactions. The following is a typical reaction mixture (weights and volumes were chosen to give 10 to 200 ppm by weight porphyrin solutions which were easy to monitor by UV-vis spectroscopy): 0.0024 g VO(etio) were dissolved in 20 ml of 1-MN, toluene, DMF, or CH₂Cl₂ and heated to the appropriate reaction temperature with a constant control heating mantle (J-KEM Scientific Model 210). The starting concentration was then determined by UV-vis spectroscopy. Approximately 0.04 ml (~100 mole equiv.) of the ligand or reagent were added. Aliquots of the reaction mixture were taken at various times to primarily monitor the disappearance-appearance of the porphyrin species.

Analyses. The fractions were examined for porphyrin content by UV-vis and second derivative UV-vis spectroscopy utilizing an HP 8452A diode array system. The spectra were collected as zero order using maximum integration time. Second derivative spectra were calculated after averaging. The entire fraction was dissolved in either CH₂Cl₂ or toluene. The amount of solvent was determined by diluting the sample so the spectral region less than 380 nm was on scale. This ranged from 25 to 100 ml in most cases.

Results and Discussion

Screening Studies. Most reagents were tested using vanadyl etio porphyrin (VO(etio)) and watching the characteristic UV-vis spectrum change. The most effective reagents were found to be maleic acid in dimethylformamide (DMF), montmorillonite in 1-methyl naphthalene (1-MN), CF₃SO₃H in 1-MN, and FSO₃H in 1-MN, with the fastest (maleic acid at 100 mole equivalents) completely reacting with VO(etio) in 10 min. or less.

These agents were found through the testing of many different types of chemical agents, having functional groups, chelating ability, and oxidation-reduction properties. Table 1 shows an example of test data using carboxylic acids and mixtures as the reactants. The results for all materials used in the screening studies are summarized:

- Amino-carboxylate compounds: nitrilotriacetic acid works well in DMF
- Polyamino compounds: none
- Dithiocarbamates: none
- Carboxylic acid compounds: malic, benzoic, maleic, and malonic work well in DMF
- Clays: montmorillonite works well in 1-MN
- Catechol compounds: none
- Coumarin works well in DMF
- Amino-N-oxides: none
- S²⁻ does not work
- Hydroperoxides: *t*-butyl and cumene work well in DMF
- Peroxyacetic acid works very well in methylene chloride
- Oxo-titanium compounds: none
- Superacids: fluoro- and trifluoromethane sulfonic acids work well in 1-MN

Solvent effects were found for most agents tested also. Most exhibited some activity in DMF, while little or no activity in 1-MN. The agents tested in methylene chloride also generally showed excellent activity.

Table 1. Screening Studies on the Reactivity of Carboxylic Acids with VO(etio)

Reactant	Solvent System	Time Reacted	Temperature ° C	% P Removed
Tartaric	DMF	1.5 h	153	NR
Triethyl citrate	DMF	2 h	120	50
Triethyl citrate	<i>o</i> -xylene	3 h	142	NR
	<i>o</i> -xylene	18 h	142	NR
+ diethanol amine	1-MN	24 h	NA	NR
Succinic	1-MN	1 h	160	NR
	1-MN	2.5 h	222	NR
Malic	DMF	21 h	NA	99
+ quinoline	1-MN	24 h	189	18
Oxalic	DMF	24 h	153	NR
2-Ethylhexanoic	DMF	30 m	146	NR
+ air	DMF	1 h	130	NR
Fumaric	DMF	30 m	145	23
Benzoic	DMF	3.5 h	153	100
Benzoic	<i>o</i> -xylene	3 h	126	NR
	<i>o</i> -xylene	18 h	142	NR
+ HMTA	1-MN	8 h	184	28
+ diethanolamine	1-MN	24 h	NA	NR
Maleic	DMF	10 m	153	100
Maleic Anhydride	DMF	1 h	132	58
Malonic	DMF	24 h	153	100

HMTA = hexamethylenetetraamine

Superacid Reactions. A more detailed examination of the effectiveness of low concentrations of the superacids, fluorosulfonic acid (FSA) and trifluoromethane sulfonic acid (TFMSA), as demetallation agents for nickel and vanadium porphyrin compounds was conducted. Superacids were found to be extremely effective in demetallating vanadyl etio (VO(etio)) and nickel (Ni(etio)) etio porphyrin screening compounds as shown above. For examples, almost complete reaction was observed for VO(etio) in toluene at 72°C and 100 mole equivalents of TFMSA at 3 min. reaction time, while only 30% reaction was observed with CF₃COOH (another recognized strong acid) under similar conditions at 60 min. reaction time. Figure 1 shows the test results for TFMSA at 200 mole equivalent.

The porphyrin fractions isolated from Hondo 650°F⁺ and Kern River 650°F⁺ residua took 600 mole equivalents and 45 min. at 79°C for essentially complete reaction. Only 60% reaction of the petroporphyrins could be attained using 600 mole equivalents at room temperature.

The mechanism of reaction appears to be dependent on the porphyrin species. The behavior of VO(etio) with TFMSA suggests an adduct-type compound is formed first which then goes on to form demetallated and other products. The adduct-type compound appears to regenerate VO(etio) upon reaction with acidic water. Ni(etio) and H₂etio were found to immediately produce the non-metallated porphyrin dication, H₄etio⁺², with no evidence of unreacted porphyrin. The reaction of VO(TPP) with TFMSA exhibited evidence of the H₄TPP²⁺.

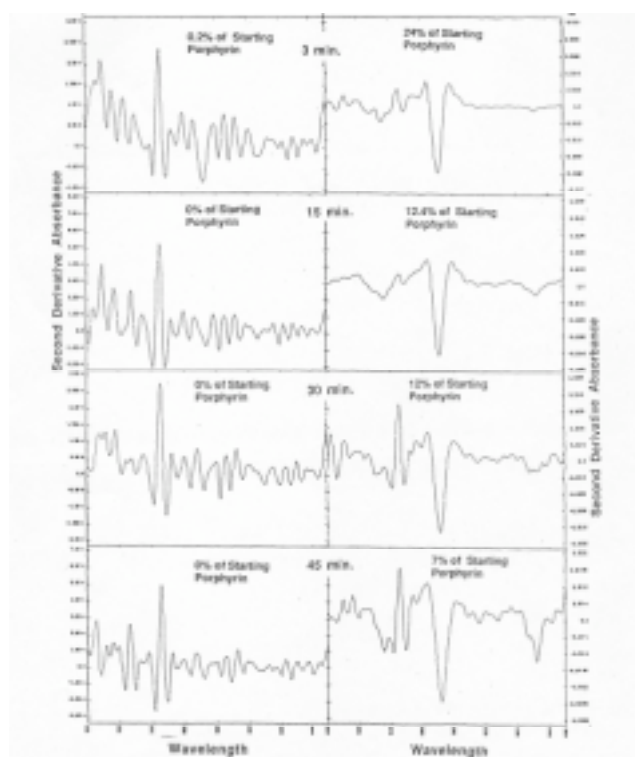


Figure 1. Second derivative UV-vis spectra of the reaction of VO(etio) porphyrin with 200 mole equivalents of TFMSA in toluene at 72°C. The y-axis is the second derivative relative absorbance. The Figures on the left side are the spectra after reaction and the figures on the right side are the corresponding spectra after water wash.

Acknowledgement.

This work was funded through a CRADA between Phillips Petroleum Company and LLNL. This work was performed under the auspices of the U. S. Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

References

1. Schuetze, B. and Hofmann, H., *Hydrocarbon Processing*, 1984, **63**(2), 75-82.
2. Richman, J. E., and Atkins, T. J., *J. Am. Chem. Soc.*, 1974, **96**(7), 2268-2270.